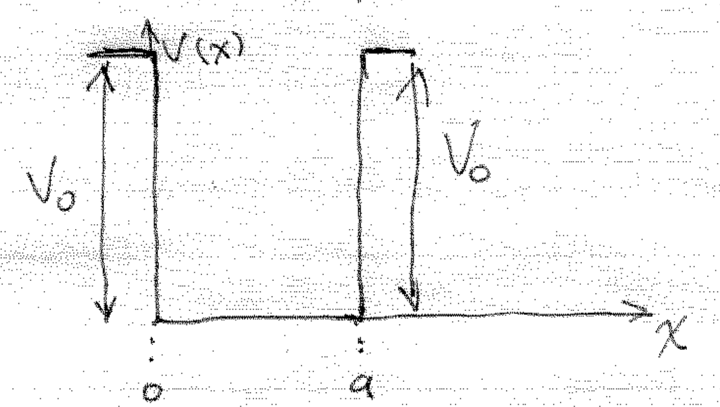
Lecture 7: The Time Dependent Schrödinger Equation

The infinite square well:

The most basic problem beyond the free particle is the "infinite square well", i.e. a particle in a 1D "box" with impenetrable walls



Drawn here is a "finite" square well of depth V_0. Here we consider $V_0 \to \infty$. Given a finite total energy, there is zero probability to have $V = \infty$.

$\Rightarrow$ The wave function must be zero for $x < 0$, $x > a$.

Boundary conditions:

Given finite momentum, $\Psi(x)$ must be continuous

$$\Rightarrow \Psi(x=0) = \Psi(x,a) = 0$$

These boundary conditions are crucial for determining the solutions to the T.I.S.E.

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Consider then $V(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$

In the well, the general solution is that of a free particle

$$\Rightarrow \quad \psi(x) = A e^{ikx} + B e^{-ikx}$$

where $\frac{(\hbar k)^2}{2m} = E$

Given boundary condition $\psi(x=0) = 0 \Rightarrow A = -B$

$$\Rightarrow \psi(x) = A\left(e^{ikx} - e^{-ikx}\right) = 2i A \sin kx = A' \sin kx$$

Given boundary condition $\psi(x=a) = 0$

$$\Rightarrow A' \sin ka = 0 \quad \Rightarrow \quad k_n a = n\pi \Rightarrow k_n = n\frac{\pi}{a}$$

$n = 1, 2, 3, \ldots$

$$\Rightarrow \boxed{E_n = \frac{(\hbar k_n)^2}{2m} = n^2 \frac{\hbar^2 \pi^2}{2ma^2}}$$

Because of the boundary conditions, the energy is quantized. We saw this in the first lecture. the deBroglie hypothesis explained Bohr's stationary state hypothesis as the normal modes of oscillation of waves confined to a circular orbit.

$$\Rightarrow \frac{|A_n'|^2}{k_n}\int_0^{ka}\sin^2\theta\, d\theta = \frac{|A_n'|^2}{\frac{n\pi}{a}}\underbrace{\int_0^{n\pi}\sin^2\theta\, d\theta}_{n\pi/2} = 1$$

$$\therefore\ |A_n'|^2 = \left(\frac{a}{2}\right)^{-1} \Longrightarrow A_n' = \sqrt{\frac{2}{a}}\, e^{i\phi}.$$

<u>Note:</u> the phase ϕ is <u>arbitrary</u>. The <u>overall phase</u> of the wave function has no influence on the probabilities, e.g. $|\psi(x,t)|^2$.

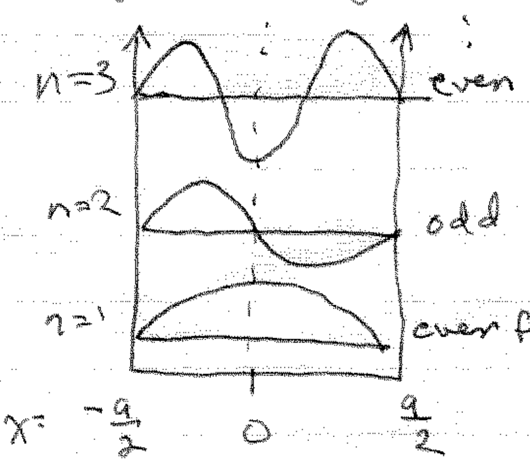
Here we choose the overall phase $\phi = 0$ (real state)

$\therefore$ The stationary states: $\psi_n(x,t) = u_n(x)\, e^{-i\omega_n t}$

$$u_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) & 0 \le x \le a \\ 0 & \text{otherwise} \end{cases}$$

$$E_n = \hbar\omega_n = \frac{n^2\pi^2}{2ma^2}$$

<u>Symmetric case:</u> Sometimes it is useful to place the potential symmetrically about the origin.



$$u_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right) & n = 1, 3, 5 \ldots \quad \text{even fnct.} \\ \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) & n = 2, 4, 6 \ldots \quad \text{odd fnct.} \end{cases}$$

Beyond stationary states:

Consider the superposition of two different stationary states.

$$\Psi(x,t) = c_1 \psi_1(x,t) + c_2 \psi_2(x,t)$$

where c_1 and c_2 are arbitrary complex #'s.

By the linearity of the P.D.E., this is a solution to the Schrödinger eq.

$$\frac{\hbar}{-i}\frac{\partial}{\partial t}\Psi = c_1\left(-\frac{\hbar}{i}\frac{\partial}{\partial t}\psi_1\right) + c_2\left(-\frac{\hbar}{i}\frac{\partial}{\partial t}\psi_2\right)$$

$$= c_1(\hat{H}\psi_1) + c_2(\hat{H}\psi_2)$$

$$= \hat{H}(c_1\psi_1 + c_2\psi_2)$$

$$\Rightarrow -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) \quad \checkmark$$

Consider then the probability density

$$|\Psi(x,t)|^2 = |c_1\psi_1(x,t) + c_2\psi_2(x,t)|^2$$

$$= |c_1|^2 |u_1(x)|^2 + |c_2|^2 |u_2(x)|^2$$

$$+ 2\,\mathrm{Re}\left(c_1 c_2^* u_1(x) u_2^*(x)\, e^{-i(\omega_1-\omega_2)t}\right)$$

In ~~our~~ our case we have choosen $u_n(x)$ real

$$\Rightarrow |\Psi(x,t)|^2 = |c_1|^2 u_1^2(x) + |c_2|^2 u_2^2(x)$$

$$+ 2u_1(x)\, u_2(x)\, \mathrm{Re}\left(|c_1||c_2|\, e^{-i[(\omega_1-\omega_2)t + \phi_2 - \phi_1]} \right)$$

where $c_i = |c_i|\, e^{i\phi_i}$

$$\Rightarrow \boxed{\begin{aligned} |\Psi(x,t)|^2 &= |c_1|^2 u_1^2(x) + |c_2|^2 u_2^2(x) \\ &\quad + 2u_1(x)\, u_2(x) \cos(\Delta\omega_{12} t - \Delta\phi) \\ &\text{where } \Delta\omega_{12} = \omega_1 - \omega_2 \qquad \Delta\phi = \phi_1 - \phi_2 \end{aligned}}$$

This probability density changes with time with a frequency $\Delta\omega_{12} = |\omega_1 - \omega_2|$. The relative phase between terms is physical — i.e. it determines the probability

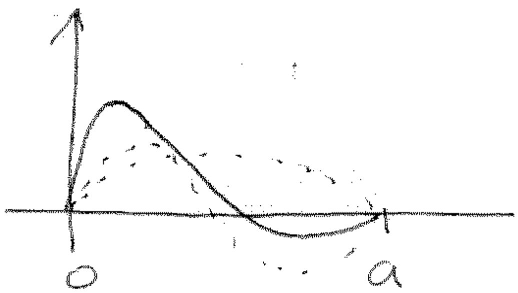
Example : let $c_1 = c_2 = \frac{1}{\sqrt{2}}$ (We'll see why this choice makes sense soon)

$$\Psi(x,t) = \frac{1}{\sqrt{2}} u_1(x)\, e^{-i\omega_1 t} + \frac{1}{\sqrt{2}} u_2(x)\, e^{-i\omega_2 t}$$

$$= \frac{1}{\sqrt{a}} \left(\sin\left(\frac{\pi x}{a}\right) e^{-i\omega_1 t} + \sin\left(\frac{2\pi x}{a}\right) e^{-i\omega_2 t} \right)$$

$$= \frac{1}{\sqrt{a}} e^{-i\omega_1 t} \left(\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right) e^{-i\omega_{21} t} \right)$$

$t=0$: $\psi(x,0) = \frac{1}{\sqrt{2}}\left(\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right)$

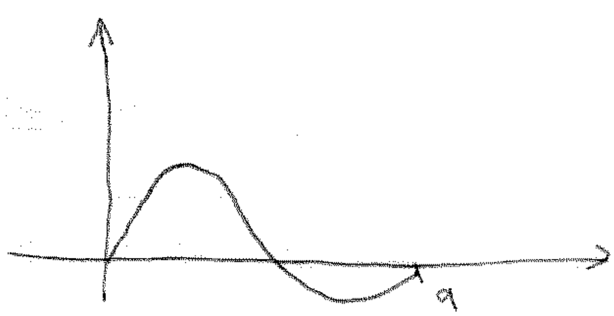


← overall phase irrelevant

$t_\pi = \frac{\pi}{\Delta\omega_{12}}$ $\psi(x,t) = \frac{e^{-i\omega_1 t_\pi}}{\sqrt{a}}\left(\sin\left(\frac{\pi x}{a}\right) - \sin\left(\frac{2\pi x}{a}\right)\right)$

← irrelevant

$t_{2\pi} = \frac{2\pi}{\Delta\omega_{12}}$ $\psi(x,t) = \frac{e^{-i\omega_1 t_{2\pi}}}{\sqrt{2}}\left(\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right)$



Thus, the wave function oscillates in shape with a period $T = \frac{2\pi}{\Delta\omega_{12}}$

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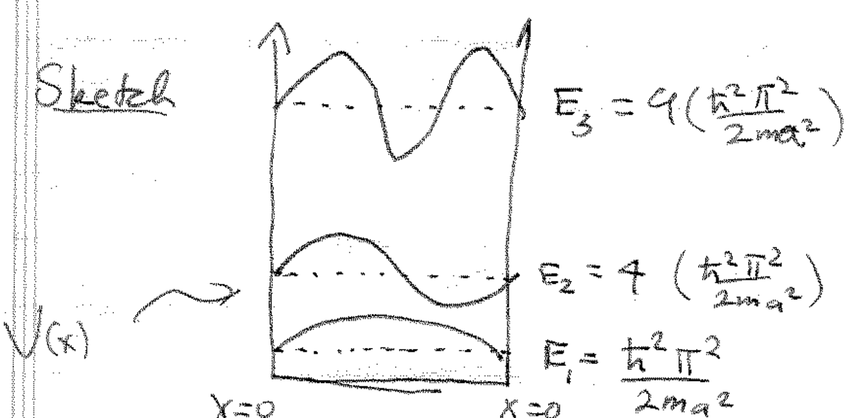
Sketch



These are the familiar normal modes of a string pinned between two rigid walls.

Note: The lowest energy state E_1 has $E_1 > 0$. This is known as "zero point energy". This can be understood from the uncertainty principle. Because of the localization $\Delta x = a \Rightarrow \Delta p \sim \frac{\hbar}{a}$

Thus, the lowest possible energy = ground state

$$E_{ground} \sim \frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2ma^2}$$

Thus the stationary state solutions

$$\Psi_n(x,t) = u_n(x)\, e^{-i\omega_n t} = A_n' \sin(k_n a)\, e^{-i\omega_n t}$$

where $E_n = n^2\left(\frac{\hbar^2}{2ma^2}\right)$ $n, 1, 2, 3$

To determine A_n' we use normalization.

$$1 = \int_{-\infty}^{\infty} |\Psi_n(x,t)|^2\, dx = \int_{-\infty}^{\infty} |u_n(x)|^2\, dx = |A_n'|^2 \int_0^a \sin^2(kx)\, dx$$

Normalization for superposition:

$t=0$ $\quad \Psi(x) = c_1 u_1(x) + c_2 u_2(x)$

$$|\Psi(x)|^2 = |c_1|^2 |u_1(x)|^2 + |c_2|^2 |u_2(x)|^2$$
$$+ \; c_1^* c_2 \; u_1^*(x) u_2(x) + c_2^* c_1 \; u_2^*(x) u_1(x)$$

Require $\int_{-\infty}^{\infty} |\Psi(x)|^2 \, dx = 1$

$$\Rightarrow \int_{-\infty}^{\infty} dx \, |\Psi(x)|^2 = |c_1|^2 \underbrace{\int_{-\infty}^{\infty} dx \, |u_1(x)|^2}_{=1} + |c_2|^2 \underbrace{\int_{-\infty}^{\infty} dx \, |u_2(x)|^2}_{=1}$$
$$+ c_1^* c_2 \int_{-\infty}^{\infty} dx \; u_1^*(x) u_2(x) + c_2^* c_1 \int_{-\infty}^{\infty} dx \; u_2^*(x) u_1(x)$$

Aside $\int_{-\infty}^{\infty} dx \; \underset{\text{real}}{u_1^*(x) \, u_2(x)} = \frac{2}{a} \int_0^a dx \; \underset{\text{even}}{\sin\left(\frac{\pi x}{a}\right)} \; \underset{\text{odd}}{\sin\left(\frac{2\pi x}{a}\right)} = 0$

$$\Rightarrow \boxed{\int_{-\infty}^{\infty} dx \, |\Psi(x)|^2 = |c_1|^2 + |c_2|^2 = 1}$$

Normalization required sum of absolute squares of "expansion coefficients" add to 1

Possible normalized states:

$$\Psi_a(x) = \frac{1}{\sqrt{2}} u_1(x) + \frac{1}{\sqrt{2}} u_2(x)$$

$$\Psi_b(x) = \frac{1}{\sqrt{2}} u_1(x) + \frac{i}{\sqrt{2}} u_2(x)$$

$$\Psi_c(x) = e^{i\frac{\pi}{4}}\sqrt{\frac{3}{5}}\, u_1(x) + e^{i\pi/8}\sqrt{\frac{2}{5}}\, u_2(x)$$

$$\Psi_d(x) = \left(\frac{1+2i}{3}\right) u_1(x) + \sqrt{\frac{5}{9}}\, u_2(x)$$

Note: the relative phase matters: interference

General superposition

Let $\Psi(x) = \sum_{n=1}^{\infty} c_n u_n(x)$

Normalization $\int_{-\infty}^{\infty} dx\, |\Psi(x)|^2 =$

$$= \sum_{n=1}^{\infty} |c_n|^2 \underbrace{\int_{-\infty}^{\infty} dx\, |u_n(x)|^2}_{=1} + \sum_{m \neq m} c_n c_m^* \int_{-\infty}^{\infty} dx\, u_m^* u_n$$

Aside $\int_{-\infty}^{\infty} dx\, u_m^* u_n = \frac{2}{a} \int_0^a dx \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right)$

$$= \frac{1}{a} \int_0^a dx \left[\cos\left(\frac{(m-n)\pi x}{a}\right) - \cos\left(\frac{(m+n)\pi x}{a}\right)\right]$$

$$= \frac{-1}{\pi} \left[\frac{1}{m-n} \sin\left[\frac{(m-n)\pi x}{a}\right] - \frac{1}{m+n} \sin\left(\frac{(m+n)\pi x}{a}\right)\right]_0^a$$

$$= 0 \quad \text{if} \quad m \neq n$$

Normalization:

$$\therefore \boxed{\int_{-\infty}^{\infty} dx\, |\Psi(x)|^2 = \sum_{n=1}^{\infty} |c_n|^2 = 1}$$

Finally, let us consider the expectation value of energy. As we saw in lecture we found the expected value of momentum

$$\langle p \rangle = \int dx\, \psi^*(x)\, \hat{p}\, \psi(x)$$

operator in position-space $\frac{\hbar}{i}\frac{\partial}{\partial x}$

Since the Hamiltonian in the operator for energy

$$\langle E \rangle = \int dx\, \psi^*(x)\, \hat{H}\, \psi(x)$$

where $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

If $\psi(x) = u_n(x)$: energy eigenstate, stationary state

$$\hat{H}\psi = E_n\psi \Rightarrow \langle E \rangle = E_n$$

Now $\langle E^2 \rangle = \int dx\, \psi^*(x)\, \hat{H}^2 \psi(x)$

$$= E_n^2 \int dx\, |\psi|^2 = E_n^2$$

Variance $\Rightarrow \Delta E^2 = \langle E^2 \rangle - \langle E \rangle^2 = E_n^2 - (E_n)^2$

$$= 0$$

$\Rightarrow$ The energy eigenstates have no uncertainty in E

For general superposition:

$$\Psi(x) = \sum_n c_n u_n(x)$$

$$\langle E \rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x)\, \hat{H}\, \Psi(x)$$

$$= \sum_{n,m} c_n^* c_m \int_{-\infty}^{\infty} dx\, u_n^*(x)\, \underbrace{\hat{H}\, u_m(x)}_{=E_m}$$

$$= \sum_{n,m} c_n^* c_m E_m \int_{-\infty}^{\infty} dx\, u_n^*(x)\, u_m(x)$$

Aside: $\int_{-\infty}^{\infty} dx\, u_n^*(x) u_m(x) = \begin{cases} 0 & n \neq m \\ 1 & n = m \end{cases}$

$$\equiv \delta_{n,m} = \text{"Kronecker delta"}$$

$$\therefore \langle E \rangle = \sum_{n,m} c_n^* c_m E_m \delta_{n,m}$$

$$\Rightarrow \boxed{\langle E \rangle = \sum_n |c_n|^2 E_n}$$

This expected value has a familiar form:

$$\langle E \rangle = \sum_n P(E_n) E_n$$

where $\boxed{P(E_n) = |c_n|^2 = \text{Probability to find energy } E_n}$

Normalization: $\sum_n P(E_n) = \sum_n |c_n|^2 = 1$ ✓